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Eur pälsch s Patentamt  
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(11) Publication number:

**0 359 432 B1**

(12)

## EUROPEAN PATENT SPECIFICATION

- (45) Date of publication of patent specification: **23.02.94** (51) Int. Cl.<sup>5</sup>: **C08F 6/10, B01D 3/06, B01D 1/06**
- (21) Application number: **89308690.0**
- (22) Date of filing: **29.08.89**

(54) **Devolatilization of liquid composition containing polymer and volatile constituents.**

(30) Priority: **29.08.88 JP 214075/88**

(43) Date of publication of application:  
**21.03.90 Bulletin 90/12**

(45) Publication of the grant of the patent:  
**23.02.94 Bulletin 94/08**

(64) Designated Contracting States:  
**DE ES FR IT**

(56) References cited:  
**BE-A- 679 727**  
**GB-A- 2 126 116**  
**US-A- 4 699 976**

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**EP 0 359 432 B1**

## Description

This invention relates to devolatilization apparatus for a first step of equipment for manufacturing thermoplastic resins such as styrene polymers to remove continuously and efficiently unreacted monomer, solvent and like volatile substances from a liquid composition containing polymer and volatile constituents (hereinafter referred to as polymer solution) and a method for devolatilization using the same apparatus.

Usually, when causing bulk or solution polymerization of styrene, either alone or together with other copolymerizable monomers, the polymerization reaction is discontinued when polymerization of 40 to 90% by weight of monomer is obtained and unreacted monomer remaining in the resultant polymer solution, and solvent and like volatile substance also remaining in the solution in the case of the solution polymerization, are separated. Particularly, low residual volatile component content is required in the case of styrene polymer used for food containers or the like. When performing a devolatilization operation, in order to obtain a satisfactory polymer quality it is important to pay attention lest the polymerization proceeds excessively and also lest the polymer solution should be exposed to a high temperature for a long time, thus avoiding quality deterioration due to otherwise possible generation of low molecular weight polymers or crosslinking with rubber phase in the case where a rubber component is contained.

An apparatus for removing volatile components of a styrene-based polymer solution usually comprises a heat exchanger for giving the polymer solution an amount of heat necessary for the evaporation of the volatile components and also heating the polymer solution after the evaporation of the volatile components to maintain adequate fluidity of the polymer, a devolatilizer for causing evaporation of volatile components contained in the polymer solution and vacuum means. To obtain high quality polymer, i.e., to reduce quality degradation of polymer under a high temperature condition, it is desired to minimize the distance between the heat exchanger and devolatilizer, increase the surface area of the polymer solution per unit volume in the devolatilizer and increase the amount of evaporation of the volatile components. As apparatus with a minimum distance between the heat exchanger and devolatilizer, US-A-4537954 and US-A-4699976 disclose structures in which a vertical multi-tube heat exchanger for heating polymer solution taken out from a polymerization process is disposed on a devolatilizer to permit the polymer solution having passed through the heat exchanger to flow down immediately into the devolatilizer while forming bubbles. The prior art noted above also propose to

add, in the use of the apparatus, a bubble-forming agent such as water or alcohol to the polymer solution to improve the devolatilization efficiency.

However, in the disclosed apparatus the evaporation surface area of the polymer solution is limited by the number and diameter of the heat exchanger tubes. This means that a limit is imposed on the reduction of the amount of volatile components remaining in the polymer solution after the devolatilization treatment. If it is intended to elevate the temperature of the polymer solution to reduce the content of the residual volatile components, low molecular weight polymer will be produced to degrade the quality of polymer. It is proposed to perform devolatilization in two or three steps in order to solve the above problem. With this method, however, sufficient effects cannot be obtained.

According to a first aspect of the present invention there is provided an apparatus for devolatilizing a liquid composition containing polymer and volatile constituents, the apparatus comprising a heat exchanger, a volatilizer coupled to the underside of said heat exchanger and vacuum means connected to said volatilizer, characterised in that said apparatus further comprises a distributor provided between said heat exchanger and said volatilizer.

According to a second aspect of the present invention there is provided a method of devolatilizing a liquid composition containing polymer and volatile constituents using a devolatilization apparatus in accordance with the first aspect of the present invention.

The hereinafter described embodiments of the present invention provide an apparatus and a method for devolatilizing polymer solution, i.e., liquid composition containing polymer and volatile constituents, which permit reduction of the concentration of residual volatile components in the polymer solution to 300 ppm or below without need of any great equipment investment or energy consumption.

The choice of heat exchanger type is not particularly restricted so long as the heat exchanger can heat the polymer solution. However, a vertical multi-tube heat exchanger may suitably be used. Where the content of unreacted monomer, solvent and other volatile constituents is 1% by weight or above, a suitable heat exchanger to be used may have a structure, in which a plurality of static mixing elements, free from any moving parts, are provided in each tube for mixing the polymer solution and preventing channelling. Where the content of volatile constituents is not higher than 1% by weight, a heat exchanger without any mixing element is suitable because of increased pressure rise in the tube. However, should a plurality of mixing

elements be provided, these may be used to mix the polymer solution by repeating the splitting of the stream of polymer solution entering the tube, changing the direction of flow and direction of splitting and joining the split streams. Examples of such a mixer are a SULZER-type tubular mixer and a KENIX-type static mixer.

The distributor design is not particularly restricted, so long as it can distribute the flow path of polymer solution and withstand pressure received at the time of the distribution. As an example, the distributor may be plate-like with a number of slits or holes of other shapes. The shape of the holes is not restricted. As examples, the holes may be slit-like, circular polygonal, triangular, star-shaped, parallelogram-shaped and gourd-shaped. Theoretically, it is preferred that the area of the holes reduces progressively in the downstream direction of the flow of polymer solution. In view of the balance between the cost of processing and performance, however, circular holes having a constant section are suitable.

The size, number and arrangement of the distributor holes, which may be slit-like, circular, etc., should be such that the surface area of polymer solution appearing from the distributor is greater than the surface area of polymer solution when it is forced directly out from the heat exchanger into the devolatilizer at the same flow rate, and also that no excessive pressure be applied to the distributor. Further, ideally no substantial difference in speed velocity should be produced between the polymer solution streams passing through the different holes. For example, when using a vertical multi-tube heat exchanger with a tube inner diameter "a" between 10 and 50mm and a distributor having circular holes, the diameter "b" of the circular hole is ideally selected to be in the range of  $3 < a/b < 10$ . Specifically, each tube is suitably provided with 4 to 10 circular holes, each with a diameter of between 3 and 5mm. In addition the holes are advantageously arranged within the central portion of the distributor as this permits uniform velocity of the polymer solution streams through the individual holes to be readily obtained.

The distributor may be mounted in any suitable way. As an example, it may be mounted on a tube plate of the heat exchanger by using steel bars, support plates and bolts or it may be mounted directly, such as by welding, on each of the outlet ends of the heat exchanger tubes.

Of these methods of mounting, the latter method permits polymer solution streams emerging from the individual heat exchanger tubes to be led directly, i.e., without joining together, to the distributor. Thus, in this case it is possible to readily obtain uniform polymer solution stream velocity at the distributor outlet. In addition, it is

possible to distribute polymer solution for devolatilization by maintaining the state of mixing of polymer solution in the heat exchanger. This is desired in view of suppressing variations or reduction of the devolatilization efficiency.

In the former method of mounting, the polymer solution streams appearing from the individual heat exchanger tubes are joined together before being led to the distributor. Therefore, compared to the latter method there is a greater possibility of lack of uniformity of velocity of the distributed polymer solution streams from the distributor. Also, there is a greater possibility of changes in the state of polymer solution, for instance separation of part of a bubble-forming agent from the polymer solution, due to such causes as reduction of pressure when the polymer solution streams emerging from the heat exchanger are joined together. To reduce or eliminate these possibilities, the distance between the tube plate and distributor is ideally kept to 40mm or below so that the volume defined by the tube plate and distributor is 10% or less of the total volume of the heat exchanger.

The volatilizer according to the invention is coupled to the underside of the heat exchanger and it is also connected to vacuum means, which may consist of a vacuum pump or the like, for producing a vacuum or a reduced pressure in the volatilizer. As an example, the vacuum pumps may be one of a sort which is usually used in an apparatus for manufacturing styrene-based resin. Ideally the vacuum means is one which can hold a volatilizer inner pressure of  $1.3 \times 10^3$  to  $1.3 \times 10^4$  N.m<sup>-2</sup> (10 to 100 mmHg).

The devolatilization apparatus includes a distributor provided between a heat exchanger and a volatilizer. As polymer solution flowing down from the heat exchanger passes through the distributor, the shape of the polymer is changed to one having a large surface area, for instance, a film-like, a plate-like or a thin bar-like form, suitable for devolatilization, and in this shape it is supplied directly to the volatilizer and then subjected to bubble formation. As a result, the devolatilization efficiency is significantly improved. Ideally, heat retaining tubes are provided in the volatilizer. In this case, polymer solution supplied to the volatilizer is temporarily received and heated by the heat retaining tubes before falling. Thus, the devolatilization efficiency can be improved further.

The devolatilization apparatus can be used for devolatilizing thermoplastic polymer solutions containing unreacted monomer, solvent and other volatile constituents. It is particularly suited for use in the devolatilization of styrene-based polymer solutions, which solutions may or may not be rubber-modified. It is particularly suitable for devolatilization of styrene-based polymer solution, either rub-

ber-modified or not, obtained by performing polymerization until a comparatively high polymerization conversion of 80 to 95% by weight is obtained. For it is possible to obtain efficient volatilization in a state, in which low molecular polymer can be difficultly produced.

As an example, prior to carrying out the method according to the present invention, (1) polymer solution with a polymerization conversion of 40 to 90% by weight may be devolatilized until the volatile constituent content is 1% by weight or below by using one or two stages of a prior art devolatilization apparatus for polymer solution. A bubble-forming agent, such as water or alcohol may then be added, if necessary, and devolatilization then performed under conditions of a temperature of 200 to 270 °C and volatilizer inner pressure of  $2.7 \times 10^3$  to  $4.0 \times 10^3$  N.m<sup>-2</sup> (20 to 30 mmHg), for instance, using a polymer solution volatilizer according to the present invention. As another example of carrying out the method according to the invention, (2) polymer solution with a polymerization conversion of 80 to 95% by weight may be devolatilized until the volatile constituent content is 1% by weight or below, preferably 0.2 to 0.5% by weight, by using one or two stages of the polymer solution devolatilization apparatus according to the invention, preferably one including a heat exchanger with a plurality of static mixing elements without any moving parts provided in each tube and under conditions of a temperature of 200 to 250 °C and a pressure of  $1.3 \times 10^3$  to  $1.3 \times 10^4$  N.m<sup>-2</sup> (10 to 100 mmHg), then a bubble-forming agent such as water or alcohol is added, if necessary, and then performing volatilization in the same way as in the example (1). The bubble-forming agent such as water or alcohol may be added and mixed by any means. As an example, this may be done by using a tubular mixer with a plurality of inner static mixing elements without any moving parts, for instance, a SULZER-type tubular mixer or a KENIX-type static mixer. Usually, the bubble-forming agent is added in an amount of 0 to 5 parts by weight, preferably 0.5 to 3 parts by weight, to 100 parts by weight of the solid phase of polymer.

The invention will now be described in greater detail with reference to the accompanying drawings.

In the drawings:

Fig. 1 is a schematic sectional view showing an example of the apparatus for devolatilizing polymer solution according to the invention;

Figs. 2 to 5 are fragmentary enlarged-scale sectional views showing respective examples of a distributor mounting portion;

Figs. 6 to 8 are plan views showing examples of suitable shapes for distributor holes or openings; and

Figs. 9 to 13 are plan views showing examples of other shapes and arrangements of distributor holes or openings.

In the apparatus shown in Fig. 1, polymer solution is supplied from a polymerization process through a ductline 1 to a vertical multi-tube heat exchanger 2. A volatilizer 3 is coupled to the underside of the heat exchanger 2. The heat exchanger 2 has a lower tube plate 4. A distributor 5 is mounted on the lower side of the tube plate 4. The volatilizer 3 is connected to vacuum means 6 for evacuating it or reducing pressure in it. A plurality of horizontal heat retaining tubes 7, through which a heat medium can flow, are provided in the volatilizer 3 substantially at a vertically mid-way position thereof. The bottom of the volatilizer 3 is coupled to a gear pump 8 for pumping devolatilized polymer solution to a ductline 9. Static mixing elements (not shown) without any moving parts may be provided in each of tubes 10 of the vertical multi-tube heat exchanger 2.

Figs. 2 to 5 are fragmentary enlarged-scale sectional views showing examples of a mounting portion of the distributor 5.

In the example of Fig. 2, a distributor 5, having a number of holes 11, is mounted via stays 12. The stays 12 each have one end welded to the tube plate 4 of the heat exchanger 2 and the other end welded to the distributor 5. A peripheral wall 13 is welded to the outer periphery of the distributor 5, and also to the tube plate 4.

In the example of Fig. 3, a distributor 5 having a peripheral wall 13 is mounted with stay bolts 14, welded to the tube plate 4 of the heat exchanger 4, and nuts 15.

In the example of Fig. 4, a distributor 5 is directly welded to an outlet of tube 10 of the heat exchanger 2.

In the example of Fig. 5, a screw fitting 16 is welded to an outlet portion of tube 10 of the heat exchanger 2, and a distributor 5 with a screw-formed peripheral wall is mounted in the fitting 16.

The examples of Figs. 3 to 5 are suitable in that the distributor 5 can be readily removed or replaced.

Figs. 6 to 8 are plan views showing examples of the shape and arrangement of holes 11 in the distributor 5 mounted on the outlet portion of tube 10 of the heat exchanger 2. As shown, the holes are circular and their preferred arrangements are as shown in Figs. 7 and 8, in which no hole is formed in the central portion of the tube, in which portion the speed velocity of polymer solution is maximum, which helps keep the velocity of flow of polymer solution uniform.

Figs. 9 to 13 are plan views showing non-circular examples of holes 11 in the distributor 5 mounted on an outlet portion of tube 10 of the heat

exchanger 2. In the example of Fig. 9, slit-like holes are formed. In the example of Fig. 10, triangular holes are formed. In the example of Fig. 11, star-like holes are formed. In the example of Fig. 12, parallelogram-shaped holes are formed. In the example of Fig. 13, gourd-shaped holes are formed.

Comparison tests were conducted using a devolatilization apparatus (A) of the construction shown in Fig. 1, except that the temperature preservation tubes 7 were not provided and that the distributor 5 was like that shown in Fig. 4, a devolatilization apparatus (B) of the construction shown in Fig. 1, except that the temperature preservation tubes 7 were not provided and that the distributor 5 was like that shown in Fig. 2, and a contrast devolatilization apparatus (C) like that shown in Fig. 1 except that neither distributor 5 nor heat preservation tubes 7 were provided.

A monomer mixture consisting of 95% by weight of styrene and 5% by weight of toluene was polymerized until the polymerization conversion was 85% by weight and was treated using apparatus (B) like apparatus (A) except for that a plurality of static mixing elements without any moving parts are provided in each heat exchanger tube to obtain polymer solution with a volatile constituent concentration of 2,700 ppm. To the resultant polymer solution was added 2% by weight of water, and the resultant solution was mixed in a SULZER mixer SMx with static mixing elements having no moving parts. The solution was then supplied to the apparatuses (A), (B) and (C) at a rate of 3,000 litres per hour. The supplied polymer solution was elevated in temperature of 230 °C in the heat exchanger 2 with a tube inner diameter of 20mm. The polymer solution was then supplied to the volatilizer through a distributor, which had 6 holes of 3mm diameter for each heat exchanger tube, in the case of the apparatuses (A) and (B) and directly in the case of apparatus (C). In the volatilizer volatile constituents were removed by holding a volatilizer inner pressure of  $2.7 \times 10^3 \text{ N.m}^{-2}$  (20 mmHg). The volatilizer contents were then pumped out using the gear pump to obtain devolatilized polystyrene.

The residual volatile constituent concentration of polystyrene was 177 ppm in the case of using the apparatus (A), 233 ppm in the case of using the apparatus (B) and 394 ppm in the case of using the contrast apparatus (C).

#### Claims

1. An apparatus for devolatilizing a liquid composition containing polymer and volatile constituents, the apparatus comprising a heat exchanger (2), a volatilizer (3) coupled to the

underside of said heat exchanger and vacuum means (6) connected to said volatilizer, characterised in that said apparatus further comprises a distributor (5) provided between said heat exchanger and said volatilizer.

2. Apparatus as claimed in claim 1, wherein said heat exchanger (2) is a vertical multi-tube heat exchanger.

3. Apparatus as claimed in claim 2, wherein a plurality of static mixing elements, having no moving parts, are provided in each tube of said heat exchanger (2).

4. Apparatus as claimed in claim 2 or claim 3, wherein said distributor (5) is directly mounted on the outlet of each tube of said vertical multi-tube heat exchanger (2).

5. Apparatus as claimed in any of the preceding claims, wherein said distributor (5) includes arrangements of 4 to 10 circular holes (11) with diameters of between 3 and 5mm.

6. Apparatus as claimed in claim 5, wherein each arrangement of holes (11) does not include a hole (11) in a central position.

7. A method of devolatilizing a liquid composition containing polymer and volatile constituents using a devolatilization apparatus according to any preceding claim.

8. A method as claimed in claim 7, wherein said liquid composition contains styrene-based monomer.

9. A method as claimed in claim 8, wherein said liquid composition also contains 1% by weight or below of volatile constituents.

10. A method as claimed in any of claims 7 to 9, wherein said devolatilization apparatus is used in each of two stages.

11. A method as claimed in claim 10, wherein the devolatilization apparatuses of the two stages are coupled to each other via a tubular mixer including a plurality of inner stationary mixing elements having no movable portion and a bubble-forming agent is added to said liquid composition.

12. A method as claimed in any of claims 7 to 11, wherein the pressure in the volatilizer (3) is reduced to between  $1.3 \times 10^3$  and  $1.3 \times 10^4 \text{ N.m}^{-2}$  by said vacuum means.

## Patentansprüche

1. Apparatur zur Entfernung flüchtiger Bestandteile aus einer Flüssigkeit, enthaltend Polymer und flüchtige Bestandteile, wobei die Apparatur umfaßt einen Wärmeaustauscher (2), einen Verdunster (3), der mit der Unterseite des Wärmeaustauschers verbunden ist, und eine Vakuumvorrichtung (6), die mit dem Verdunster verbunden ist, dadurch gekennzeichnet, daß die Apparatur ferner umfaßt einen Verteiler (5), der zwischen dem Wärmeaustauscher und dem Verdunster angeordnet ist. 5
2. Apparatur nach Anspruch 1, wobei der Wärmeaustauscher (2) ein senkrechter Mehrrohr-Wärmeaustauscher ist. 15
3. Apparatur nach Anspruch 2, wobei eine Vielzahl von statischen Mischelementen, die keine beweglichen Teile aufweisen, in jedem Rohr des Wärmeaustauschers (2) vorgesehen ist. 20
4. Apparatur nach Anspruch 2 oder 3, wobei der Verteiler (5) direkt auf den Auslaß jedes Rohr des senkrechten Mehrrohr-Wärmeaustauschers (2) montiert ist. 25
5. Apparatur nach einem der vorangehenden Ansprüche, wobei der Verteiler (5) Anordnungen von 4 bis 10 kreisförmigen Löchern (11) umfaßt mit Durchmessern zwischen 3 und 5 mm. 30
6. Apparatur nach Anspruch 5, wobei jede Anordnung von Löchern (11) kein Loch (11) in zentraler Stellung umfaßt. 35
7. Verfahren zur Entfernung von flüchtigen Bestandteilen aus einer Flüssigkeit, enthaltend Polymer und flüchtige Bestandteile, unter Anwendung einer Apparatur zur Entfernung von flüchtigen Bestandteilen nach einem der vorangehenden Ansprüche. 40
8. Verfahren nach Anspruch 7, wobei die Flüssigkeit Monomer auf Styrolbasis enthält. 45
9. Verfahren nach Anspruch 8, wobei die Flüssigkeit außerdem 1 Gew.-% oder weniger flüchtige Bestandteile enthält. 50
10. Verfahren nach einem der Ansprüche 7 bis 9, wobei die Apparatur zur Entfernung flüchtiger Bestandteile in jeder von zwei Stufen angewandt wird. 55
11. Verfahren nach Anspruch 10, wobei die Apparaturen zur Entfernung flüchtiger Bestandteile

der beiden Stufen miteinander verbunden sind über einen rohrförmigen Mischer, umfassend eine Mehrzahl von inneren stationären Mischelementen, die keine beweglichen Teile umfassen, und wobei ein Blasen-bildendes Mittel zu der Flüssigkeit zugesetzt wird.

12. Verfahren nach einem der Ansprüche 7 bis 11, wobei der Druck in dem Verdunster (3) auf zwischen  $1,3 \times 10^3$  und  $1,3 \times 10^4 \text{ N} \cdot \text{m}^{-2}$  mit Hilfe der Vakuumvorrichtung verringert wird.

## Revendications

1. Appareillage pour enlever les constituants volatils d'une composition liquide contenant un polymère et des constituants volatils, cet appareillage comprenant un échangeur de chaleur (2), un volatiliseur (3) accouplé au côté inférieur dudit échangeur de chaleur, et des moyens (6) permettant d'établir un vide et raccordés audit volatiliseur, caractérisé en ce que ledit appareillage comprend en outre un distributeur (5) placé entre ledit échangeur de chaleur et ledit volatiliseur.
2. Appareillage conforme à la revendication 1, dans lequel ledit échangeur de chaleur (2) est un échangeur de chaleur à multiples tubes verticaux.
3. Appareillage conforme à la revendication 2, dans lequel plusieurs éléments mélangeurs statiques, sans pièces mobiles, sont placés dans chaque tube dudit échangeur de chaleur.
4. Appareillage conforme à la revendication 2 ou 3, dans lequel ledit distributeur (5) est monté directement à la sortie de chacun des tubes dudit échangeur de chaleur (2) à multiples tubes verticaux.
5. Appareillage conforme à l'une des revendications précédentes, dans lequel ledit distributeur (5) comporte des ensembles de 4 à 10 trous circulaires (11) dont les diamètres valent entre 3 et 5 mm.
6. Appareillage conforme à la revendication 5, dans lequel aucun ensemble de trous (11) ne comporte un trou (11) en position centrale.
7. Procédé pour enlever les constituants volatils d'une composition liquide contenant un polymère et des constituants volatils, à l'aide d'un appareillage de dévolatilisation conforme à l'une des revendications précédentes.

8. Procédé conforme à la revendication 7, dans lequel ladite composition liquide contient du monomère styrène.
9. Procédé conforme à la revendication 8, dans lequel ladite composition liquide contient aussi 1 % en poids de constituants volatils ou moins.
10. Procédé conforme à l'une des revendications 7 à 9, dans lequel un appareillage de dévolatilisation est utilisé dans l'un et l'autre de deux stades opératoires.
11. Procédé conforme à la revendication 10, dans lequel les appareillages de dévolatilisation des deux stades opératoires sont accouplés l'un à l'autre par l'intermédiaire d'un mélangeur tubulaire comprenant plusieurs éléments mélangeurs stationnaires internes, sans pièces mobiles, et un agent de formation de bulles est ajouté à ladite composition liquide.
12. Procédé conforme à l'une des revendications 7 à 11, dans lequel la pression régnant dans le volatiliseur (3) est réduite, à l'aide desdits moyens permettant d'établir un vide, jusqu'à une valeur située entre  $1,3 \cdot 10^3$  et  $1,3 \cdot 10^4$  N/m<sup>2</sup>.

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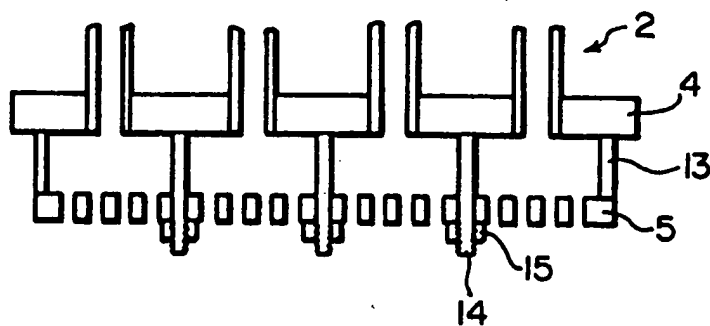
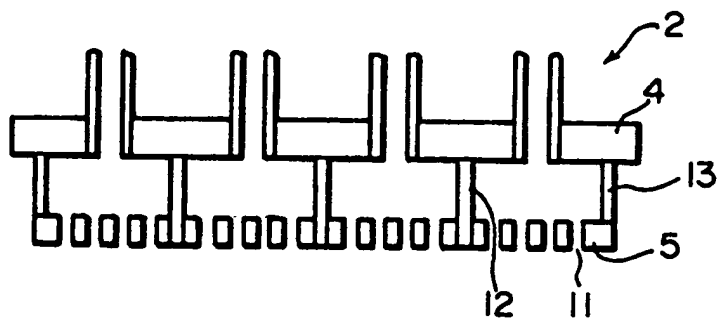
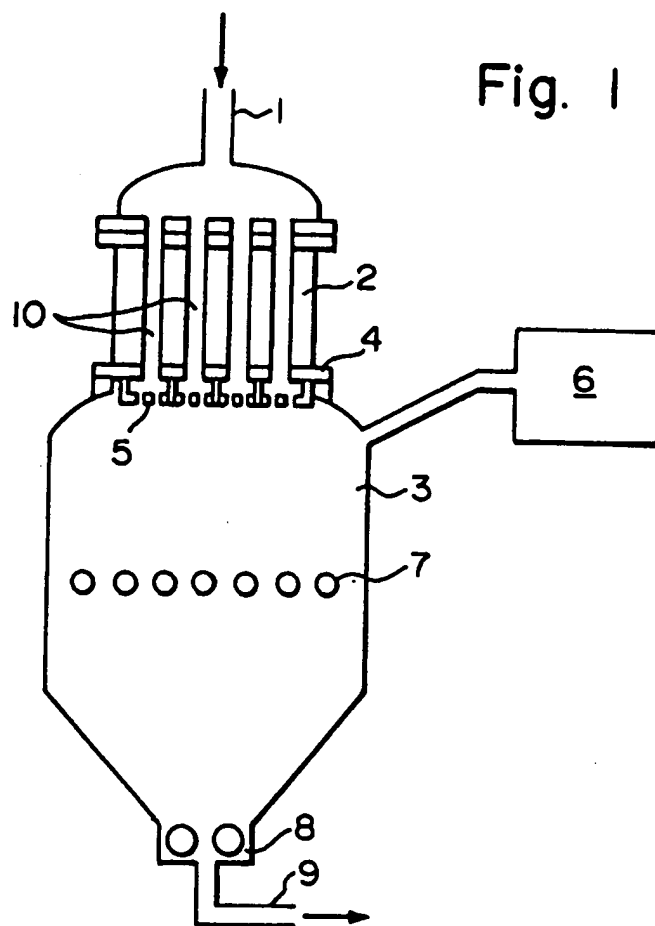




Fig. 4

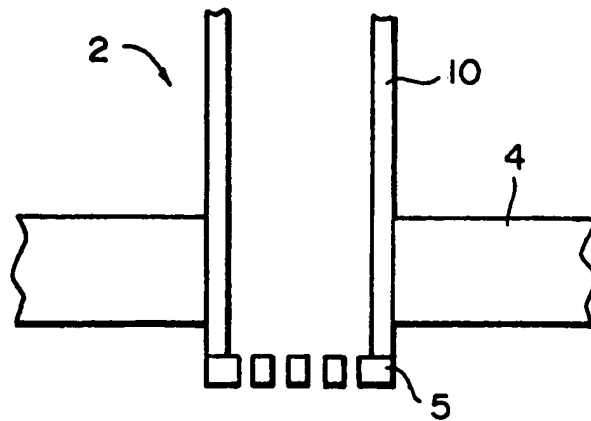


Fig. 5

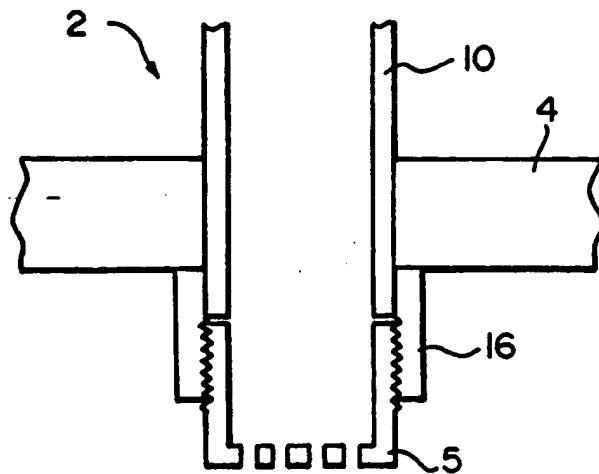


Fig. 6

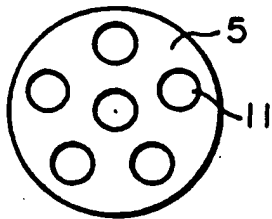


Fig. 7

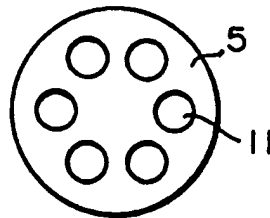


Fig. 8

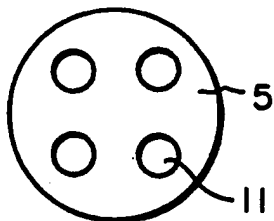


Fig. 9

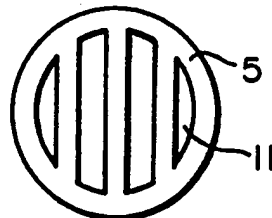


Fig. 10

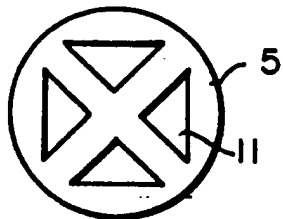


Fig. 11

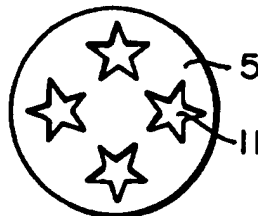


Fig. 12

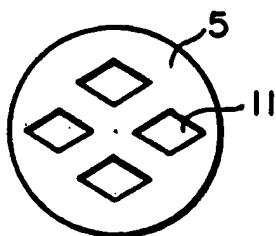


Fig. 13

